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Fish quality

STABILITY OF FISH LIPIDS DURING MICROWAVE HEATING
STABILNOŚĆ LIPIDÓW RYBNYCH PODCZAS OGRZEWANIA
MIKROFALOWEGO

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The mince from fresh fish (Baltic herring), frozen mince, mince + oat flakes, and lipids from fresh fish and from frozen mince, were heated in microwave oven for 0, 4, 8, 20, 30, and 40 min. Lipids were extracted using the Bligh-Dyer technique. Peroxide value, anisidine value, fluorescence, absorbance in UV, and sensory profile of odour and flavour were determined. Fatty acid composition was determined with a GC/MS method.

The achieved results point to the lack of a catalysing effect of microwaves on the oxidation of fish lipids contained in heated fresh fish meat, as well as during heating of lipids extracted from fresh meat. After 40 minutes of heating of mince, the amount n-3 polyunsaturated fatty acids (EPA + DHA) dropped by 18%, and in the mince with oat flakes by 10%.

INTRODUCTION

Microwave heating, in the opinion of the authors discussing this type of heat treatment (Botta et al. 1992; Kołożyn-Krajewska 1992; Brzozowska 1993; Lasen and Ovesen 1995; Grzesińska and Zawadzka-Dębska 1996), brings about smaller nutritional value losses than heating of food by conventional methods. It does not, however, guarantee microbiological safety. The attainment of culinary readiness, or heating, requires a very short time and, above all, it does not involve the absorption of a large amount of fat by the product, as is in the case of frying fish, for example (Pigott and Tucker 1990). Studies on the effect of microwave heating on food lipids are scarce. During microwave heating of soybeans, hydrolysis of triacylglycerols, as well as phospholipids, is observed. The degree of these modifications, apart from heating conditions, is considerably affected by the water content in seeds (Yoshida et al. 1995a). Microwaves used for extracting oil from rapeseeds, as com-

pared with steam, bring about the splitting of fat droplets, which facilitates their lipolysis (Ponne et al. 1996). Also in sesame seeds during microwave cooking, partial hydrolysis of lipids occurs. Concurrently, the lipids exhibit oxidative stability, which the authors ascribe to the synergism of antioxidants and non-enzymatic browning substances, formed during prolonged microwave heating, present in the seeds (Yoshida et al. 1995b). Microwave heating of distilled rape oil causes partial acceleration of its oxidation (Yoshida et al. 1993). Comparing the changes in lipids during microwave and conventional heating (oil, butter, slices of liver stewed in oil, and margarine), Farag (1994) found that microwave heating led to partial hydrolysis of lipids (acid value), and acceleration of the formation of peroxides and secondary products of oxidation (TBA). The peroxide value was twice as high as in the products heated conventionally. He also observed the degradation of fatty acids and the formation of short-chain acids. By contrast, in investigating the stability of polyunsaturated fatty acids (PUFA) in samples from four fish species of a different lipid content (among others in sardine and mackerel) during microwave cooking, Hearn et al. (1987) did not detect any decrease in fatty acids. Differences between raw and processed fish were minimal. Also Bastic et al. (1992) did not observe any reduction in PUFA during microwave heating of beef hamburgers. Regulska-Illow et al. (1996) compared the oxidation of lipids in products (soybean, pork, herring fillets) heated in a microwave oven and by conventional method, pointing to smaller oxidation of lipids during microwave heating. It is evident from the data of the above-mentioned authors, that, during cooking of herring (in water) with microwaves, the anisidine value doubles.

Nowadays, microwave ovens are considered among the most efficient types of ovens and the most rapid method for heating food items. However, the contradictory results have been reported on the heating effect of microwave energy on lipids.

The aim of this paper was to investigate the effect of microwave heating on the oxidation of fish lipids.

MATERIAL AND METHODS

The tests were conducted on Baltic herring (*Clupea harengus membras* L.). The fish had been caught in the Pomeranian Bay. Six groups of fish caught over the period from February through July were used: group 1—25 Jul 1996, group 2—25 Feb 1997, group 3—18 Mar 1996, group 4—15 Apr 1997, group 5—29 Feb 1996, and group 6—1 Apr 1996. The fish were washed, headed and gutted, washed again, dripped dry, and filleted. The fillets with skin were minced in a 2.5-mm mincer. The fish meat obtained—mince—was heated. Part of the mince from group 1 was frozen and stored for three months at a temperature of -22°C . Mince was also made of frozen whole fish after a six-month storage at -22°C . Before making the mince, the fish were thawed at around 8°C up to the temperature

allowing their preliminary processing (around -2°C). In the case of fish of group 6, the mince from fresh fish was mixed with oat flakes at a ratio of 10 : 2. Before mixing with the mince, the oat flakes were ground in a mortar. Part of the oat flakes had been previously defatted with a 2 : 1 chloroform-methanol mixture at a ratio of 20 g of oat flakes to 100 ml of solvent mixture.

Microwave heating was applied to the following:

A. Fish meat (mince):

- mince from fresh fish (3 groups of fish),
- mince from frozen fish after 3 months of storage at -22°C ,
- mince from fresh fish,
- frozen mince (from the same fish) after 3 months of storage at -22°C ,
- mince from fresh fish + oat flakes (M + F), mince + defatted oat flakes (M + Fdf), mince (control sample) (M).

The samples were heated in 20-g portions in 6-cm Petri dish.

B. Fish lipids:

- lipids from fresh fish (3 groups of fish),
- lipids from frozen mince,
- lipids from fresh fish and after a three-month storage period of extracts in a refrigerator at 9°C .

The lipids were extracted from the mince using the Bligh-Dyer method (1959) and, after evaporating the solvent, heated in portions of around 0.2 g in Petri dish.

Samples were heated in Simens oven at 60 W for 0, 2, 4, 8, 20, 30, and 40 minutes.

The following parameters were determined:

- ♦ the peroxide value (PV), using tiocyanate technique (benchmark: BN-74/A 8020-07);
- ♦ the anisidine value (AV) (IUPAC. Fifth Edition: Method II.D.26);
- ♦ fluorescence, Ex 365 nm, Em 436 nm (Fletcher et al. 1973; Kołakowska and Szczypiński 1994);
- ♦ absorbance at 350 nm;
- ♦ absorbance at 285 nm (only in selected samples);
- ♦ fatty acid composition (only in one experiment), by GC-MS method, conditions the same as in the previous paper by Kołakowska and Szczypiński (1994);
- ♦ the sensory analysis: the aroma profile according to Baryłko-Pikielna (1975). The intensity was determined on a 5-point scale for the following odours: rancid, metallic, oily, soapy, of burning, insipid, pungent, fishy, of salted fish. The evaluation was made by a team of 15 persons, checked with respect to their sensory sensitivity;
- ♦ the lipid content in the extracts was determined gravimetrically;
- ♦ the value was computed for Totox = $2 \times$ peroxide value + anisidine value (Rossell 1983).

RESULTS

Heating of the muscle lipids extracted from fresh herring (Fig. 1) brought about a decrease in oxidation products—both peroxides and aldehydes, and only after 40 minutes of heating of a thin lipid layer did a slight increase in oxidation products occur, not reaching the initial level, though.

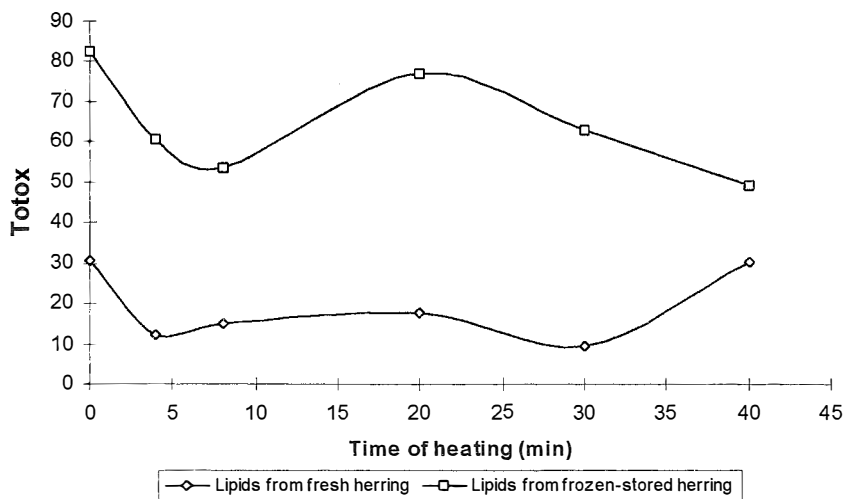


Fig. 1. Changes in lipid oxidation during microwave heating of lipids from fresh or frozen-stored herring (Totox = $2 \times$ peroxide value + anisidine value)

If, in contrast, lipids extracted from frozen-stored fish were heated (lipids that were initially considerably oxidised), then a slight increase in oxidation was observed sooner—as early as after 20 minutes of heating. Eventually, however, the oxidation level in these lipids too, did not exceed the initial level.

Heating of fresh minced fish meat brought about a decrease in the peroxide value and anisidine value, even 3–4 fold, within the first minutes of heating, as well as lack of a considerable increase in oxidation products, even during 40-minute microwave heating (Fig. 2).

When mince from the same fish after a three-month frozen-storage was heated, oxidation was at a higher level. A slight (13%), little significant, increase in the peroxide content was observed during heating. In general, however, also in this case, the total amount of oxidation products did not increase as a result of heating, even lasting 40 minutes (Fig. 2). Tests conducted on the mince from fish caught on the time-periods (Fig. 3) confirm the above-presented results—that is, lack of a catalysing effect of microwaves on lipid oxidation.

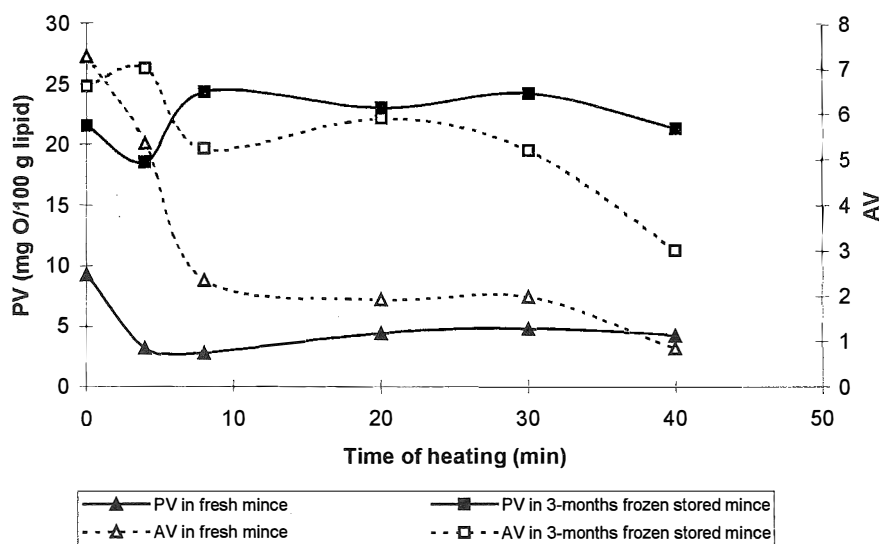


Fig. 2. Changes in peroxide value (PV) and anisidine value (AV) of lipids during microwave heating of mince from fresh or frozen-stored herring

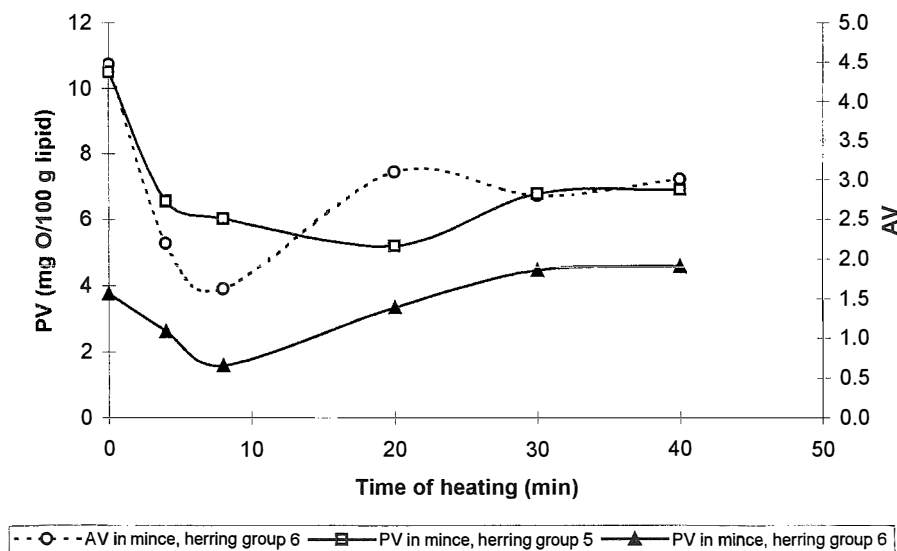


Fig. 3. Changes in lipid oxidation during microwave heating of mince from fresh herring

Neither during heating of fresh fish meat nor during heating of the extracted lipids was an increase in the fluorescence of lipids observed. By contrast, such an increase did occur when heating the meat of fish frozen-stored for a long time, or lipids from frozen fish—that is, in the cases where the lipids in the heated material were already considerably oxidised (Fig. 4).

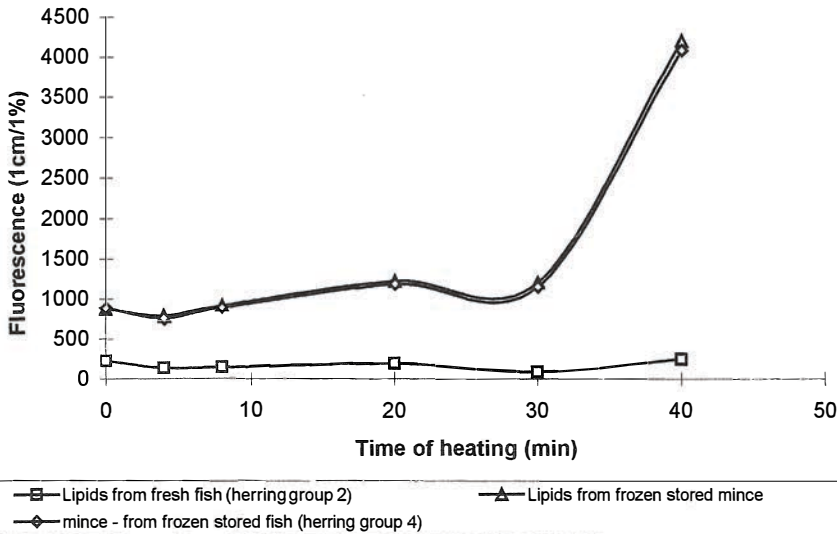


Fig. 4. Changes in fluorescence of lipids during microwave heating of lipids and mince lipids (herring group 2)

As a result of prolonged microwave heating of fish lipids, the aroma profile was poor, and the intensity of a fishy odour decreased. Even after 40 minutes of heating, no foreign odours were detected. A rancid odour at the threshold level (1 pt.) was detected by 2 out of 15 persons in the team (Fig. 5).

The addition of ground oat flakes to fish meat had an important effect on the modifications of lipids during microwave heating. Samples with oat flakes had a lower peroxide content, and a higher aldehyde content, than heated fish meat alone (Fig. 6). After 40 minutes of heating of mince with oat flakes, the amount of EPA + DHA dropped by 10%, and in the mince alone by 18.6% (Tab. 1).

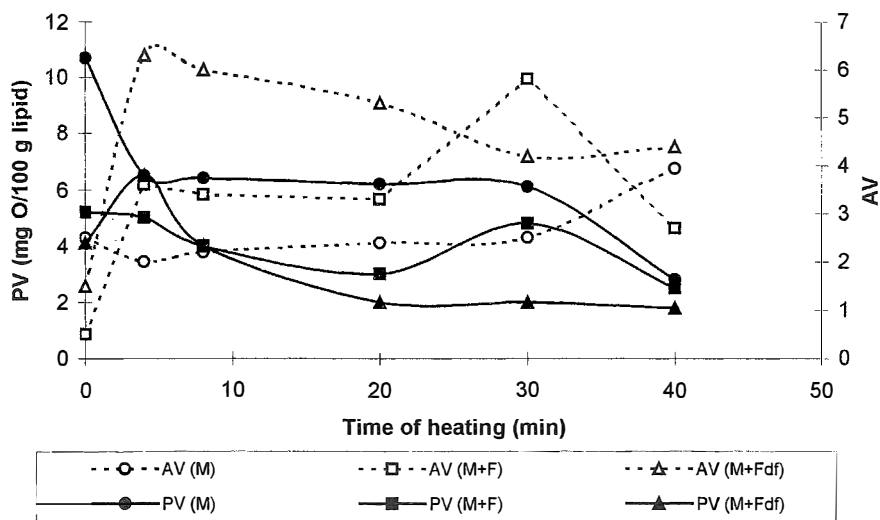


Fig. 5. Changes in lipid oxidation during microwave heating of minced fish with oat flakes (M—mince; (M + F)—mince + oat flakes; (M + Fdf)—mince + deffated oat flakes)

Table 1

Fatty acid composition in fresh mince and after 40 min. of microwave heating

Fatty acid	Before heating		After heating	
	mince	oat flakes	mince	mince + oat flakes
14 : 0	9.56	0.37	10.1	9.89
15 : 0	0.56	—	0.27	0.55
14 : 1	0.68	—	0.54	0.76
16 : 0	14.61	17.17	15.47	15.30
16 : 1	6.18	0.12	5.74	6.12
17 : 0	0.22	—	0.09	0.27
17 : 1	0.23	—	0.11	0.23
18 : 0	1.31	1.46	0.87	1.21
18 : 1	11.86	39.85	10.17	12.71
18 : 2	1.70	39.61	1.37	3.23
18 : 3	0.62	1.42	1.10	0.58
20 : 1	14.44	—	15.12	13.76
18 : 4	1.16	—	0.86	1.10
20 : 2	0.27	—	0.06	0.24
22 : 1	25.53	—	28.29	24.29
22 : 2	0.33	—	0.09	0.27
20 : 5	3.09	—	2.50	2.88
24 : 1	0.84	—	0.41	0.66
22 : 5	0.49	—	0.22	0.39
22 : 6	6.39	—	5.78	5.60

DISCUSSION

Investigations of the effect of microwave heating on fish lipids were carried out on six groups of Baltic herring caught at different dates, as herring is a fish containing lipids very susceptible to oxidation, and this susceptibility fluctuates depending upon the catch period (Kołakowska et al. 1992). The achieved results of chemical and sensory tests point to the lack of a catalysing effect of microwaves on the oxidation of fish lipids present in heated fresh fish meat, as well as during heating of lipids extracted from fresh meat.

Thereby, earlier studies and opinions on this subject have been confirmed (Hearn et al. 1987; Bastic et al. 1992). This seems to be logical as microwave energy is not capable of initiating oxidation (Kołożyn-Krajewska 1992). This action can, therefore, be viewed, above all, as the action of temperature. The maximum temperature in the heated mince was 80°C, reaching this level as early as after 2 minutes of heating, and then remaining at the same level. By contrast, heated lipids attained this temperature only after 30 minutes of heating, and then a slight increase in lipid oxidation was observed, not reaching the initial level, though.

Under the influence of microwave heating, a decrease in the amount of peroxides and aldehydes occurred, and, in the case of fresh lipids, this did not produce any noticeable effects—either in the form of an increase in absorbency or colour of lipophilous compounds measured at wavelengths of 350 or 470 nm. Heating of oxidised lipids or meat containing such lipids involved an increase in fluorescence, which may point to the reactions of non-enzymatic browning. On the model epoxyheptenal/lysine system, Zamara and Hidalgo (1995) demonstrated that, during microwave heating, the breakdown of epoxyaldehyde occurred, and a series of pyrrole derivatives of non-enzymatic browning products were formed. Concurrently, an increase in fluorescence and colour occurred.

In this work, a several-percent decrease in the amount of EPA + DHA was detected; however, this decrease relates to heating for as long as 40 minutes—that is, at least 10 times longer than is required by the attainment of culinary readiness of fish meat. This can, therefore, be treated as confirmation of the results achieved earlier by Hearn et al. (1987) on other fish species, stating that microwave heating does not bring about a decrease in PUFA.

Taking into account that herring lipids are oxidised very easily during conventional processing and storage, it can be concluded that, during microwave heating of fish, lipids contained in them are stable, and, with respect to oxidation, they do not constitute a hazard to the health quality of fish products.

CONCLUSIONS

1. Microwave heating causes decrease in the amount of peroxides and aldehydes in herring lipids. Continuous heating of fresh lipids (alone or in minced meat) does not produce new peroxides and aldehydes or other noticeable adverse effect but increase of fluorescence in not fresh lipids.
2. Losses in n-3 polyunsaturated fatty acids took place in mince after 40 minutes of microwave heating, in the mince with oat flakes were slight.
3. During microwave heating of fresh fish, lipids contained in them are stable, and with respect to oxidation, they are not hazard to health quality of fish products.

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STABILNOŚĆ LIPIDÓW RYBNYCH PODCZAS OGRZEWANIA MIKROFALOWEGO

STRESZCZENIE

Badano zmiany lipidów podczas ogrzewania mikrofalowego tkanki mięśniowej śledzi bałtyckich i samych lipidów wyekstrahowanych z tej tkanki metodą Bligha-Dyera. Ogrzewano w kuchence mikrofalowej przez 0; 4; 8; 20; 30 i 40 minut: rozdrobnioną tkankę mięśniową śledzi bałtyckich świeżych, tkankę mięśniową + płatki owsiane, tkankę mięśniową + płatki owsiane odtłuszczone, tkankę mięśniową po 3 miesiącach zamrażalniczego przechowywania, lipidy ze świeżego śledzia, mrożonego i lipidy przechowywane w postaci ekstraktów. Oznaczano poziom utlenienia lipidów (liczba nad-tlenkowa, liczba anizydynowa, fluorescencja, absorbancja w UV, ocena sensoryczna) i w wybranych próbach skład kwasów tłuszczowych metodą GC/MS. Nie stwierdzono wzrostu poziomu utlenienia lipidów podczas ogrzewania mikrofalowego tkanki mięśniowej świeżego śledzia bałtyckiego ani podczas ogrzewania samych, wyizolowanych lipidów. Po 40 min ogrzewania tkanki mięśniowej (czyli 10-krotnie dłużej niż wymaga tego osiągnięcie gotowości kulinarnej) nastąpiły straty n-3 polienowych kwasów tłuszczowych i równocześnie wzrost zawartości kwasu 22:1. Ilość kwasu ikozapenta-enowego i dokozaheksaenowego zmniejszyła się o 18%. Obecność płatków owsianych działała ochronnie. Biorąc pod uwagę, że lipidy śledzi bałtyckich bardzo łatwo ulegają utlenieniu podczas konwencjonalnego przetwarzania i przechowywania, można stwierdzić, że podczas ogrzewania mikrofalowego lipidy rybne są stabilne.

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